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(54) Lubricant compositions.

(57) Lubricant compositions, especially suitable as gear oils, containing sulphur-containing extreme pressure or anti-wear agents, are improved by incorporation of an oil-soluble salt of an amine and a weak acid or amino acid. The resulting compositions confer extended life on gears operated in them.

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LUBRICANT COMPOSITIONS

This invention relates to lubricating fluid compositions, and in particular to gear oils and to additives therefor.

High performance gear oils usually consist of a major amount of mineral oil or synthetic base stock and a minor amount of suitable additives including in particular a sulphur-containing extreme pressure or anti-wear agent. Such sulphur-containing materials are highly effective in promoting the extreme pressure and anti-wear properties of the oil and may also have valuable anti-oxidant properties. However, such sulphur-containing materials are detrimental to the environment, may cause undesirable odour, and can lead to corrosion of the metal parts with which they come in contact, especially parts containing copper.

Gear oils, for example the oils used in the gear boxes and differentials of motor vehicles, and other mechanisms involving metal on metal, for example steel on steel or steel on bronze, acting parts, are required to protect the metal surfaces and particularly the teeth of the gears. Typically, such oils remain in use for long periods without being changed. In addition to providing general lubrication, the fluid protects the loaded metal parts such as the gear teeth from damage. Gear oils are customarily tested for their ability to protect gear teeth from damage such as wear and pitting for long periods. In one system for testing such oils a gear train is run under conditions of variable and very heavy stress until the gears fail. The length of time before such failure takes place, or the wear of the gear teeth (as measured by the iron content of the fluid) becomes excessive, provides a measure of the effectiveness of the gear oil. Some current gear oils provide a measure of protection in this respect, but still further improvement is desirable.

There is therefore a need for gear lubricating oils which provide better protection of the gears and/or which contain reduced sulphur content, and for additive systems for such oils.

We have now discovered that the performance of sulphur-containing gear oils may be improved, and/or the sulphur content of such oils reduced, by incorporating in the oils a combination of a weak acid and an amine. Both acids and amines have heretofore been used in lubricating oil compositions, but the known compositions do not achieve the advantages of the present invention. For example, United States Patent No. 3398095 discloses oils containing sulphurized carboxylic acid in combination with acids and amines as so-called "vapour space inhibitors". Such oils are stated to achieve excellent corrosion inhibition for ferrous metals. They are not however suitable as gear oils. United States Patent No. 4615818 discloses that lubricant compositions comprising an oil-soluble sulphurized organic compound may be improved, so as to reduce emission of volatile sulphur compounds, by inclusion of a hindered organic amine and preferably a carboxylic acid. There is, however, no suggestion that the performance of gear oils can be improved by inclusion of the hindered amine with or without the carboxylic acid. In fact the compositions disclosed in this patent do not improve the performance of gear oils.

The present invention accordingly provides a lubricant composition comprising a lubricant, 1 to 20% by weight of one or more sulphur-containing extreme pressure or anti-wear agents soluble in said lubricant, from about 0.1 to about 10% of a weak acid and from about 0.05 to about 10% of an amine, or from 0.15 to 20% by weight of an amino-acid, the said percentages being based on the weight of lubricant the amount of said acid being from 0.2 to 2 equivalents per equivalent of the said amine, and the salt of said amine with the said acid being soluble in the said lubricant. The proportion of the said acid is usually from 0.67 to 1.25 equivalents per equivalent of the said amine.

The lubricant may be a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof, e.g. a mixture of a mineral oil and a synthetic oil. Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Middle East, North Sea and the like. Standard refinery operations may be used in processing the mineral oil.

Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid alpha olefin polymers of appropriate viscosity. Especially useful are hydrogenated liquid oligomers of C_6-C_{16} alpha-olefins, such as hydrogentated or unhydrogenated alpha-decene trimer. Alkyl-benzenes of appropriate viscosity, e.g. didodecylbenzene, can also be used.

Useful synthetic esters include the esters of monocarboxylic and polycarboxylic acids with monohydroxy alcohols and polyols. Typical examples are didodecyl adipate, trimethylolpropane tripelargonate, pentaerythritol tetracaproate, di(2-ethylhexyl) adipate, and dilauryl sebacate. Complex esters made from mixtures of mono- and di-carboxylic acids and mono- and/or polyhydric alkanols can also be used.

The compositions of the present invention can be blended into any such lubricant base stocks. The base oil is generally a mineral oil base stock such as, for example, a conventional or solvent-refined paraffinic neutral or bright stock, a hydrotreated paraffinic neutral or bright stock, a naphthenic oil, or a

cylinder oil, etc., including both straight run and blended oils. As noted above, synthetic base stocks such as for example poly-alpha-olefins with synthetic diesters in weight proportions (PAO:ester) ranging from about 95:5 to about 50:50, typically about 72:25 can be used. Generally speaking, the base stocks used in automotive gear oils range in viscosity grades from SAE 50 to 250 and preferably from 70 to 140. Suitable automotive gear oils also include cross-grades such as 75W-140, 80W-90, 85W-140, 85W-90, and the like. In general, the base stocks used in industrial gear oils have a viscosity in the range of from about ISO grade 32 to ISO grade 680 and preferably from ISO grade 68 to ISO grade 460.

The new lubricant compositions may be supplied either as finished lubricants ready for use or in the form of an additive package, i.e. a concentrate, which requires dilution with base lubricating fluid before use. As described in more detail below, the lubricant compositions of the invention may contain, in addition to the substances already mentioned, any usual additive for inclusion in such lubricants which is compatible with the sulphur-containing agent and the acid and amine. Examples of such additives are given below.

A very wide variety of sulphur-containing oil-soluble extreme pressure or anti-wear agents may be used in the compositions of the invention, and any known such agents may in principle be used. Usually the agent used contains highly active sulphur, i.e. sulphur in an amount and structural configuration such that it is capable of causing visually observable corrosive pitting of one or more gear tooth surfaces in the standard planetary spur gear test when conducted in the way described below for up to 40 hours. Examples of such agents are sulphurised olefins, sulphurised esters, sulphurised fatty acids, dialkylpolysulphides, diarylpolysulphides, dialkarylpolysulphides, sulphur, and sulphurized oils such as sulphurized sperm oil or sulphurized lard oil.

At least one of the agents used in the compositions of the present invention contains sulphur and in the preferred compositions of the invention the sulphur atoms in the sulphur containing species are highly active and generally bound directly to carbon or to more sulphur.

Whilst pitting in the standard planetary spur gear test is probably the best criterion for determining for the purpose of the present invention whether a sulphur-containing extreme pressure or anti-wear agent is or is not "highly active", another procedure which correlates reasonably well with the spur gear test can be used for this purpose. The alternative procedure is a copper coupon corrosion test which is conducted as follows: A copper coupon approximately 70 X 15 mm and about 1.25 mm in thickness is cleaned with steel wool (0000 grade), washed with heptane, and then with acetone, dried, and weighed to the nearest 0.1 mg. The cleaned coupon is placed in a test tube and covered completely with the composition to be tested, and the system is heated to 125° C in an oil bath maintained at this temperature. After holding the system at 125° C for three hours, the copper coupon is removed from the test tube, rinsed with heptane and then with acetone. The dried coupon is then rubbed with a paper towel moistened with acetone to remove any surface flakes formed by copper corrosion. The coupon is then air-dried and weighed to the nearest 0.1 mg. The difference in weight between the initial copper coupon and the coupon after the test represents the extent to which the copper has been corroded under the test conditions: the larger the weight difference, the greater the copper corrosion, and thus the more active the sulphur compound. For the purposes of this invention a sulphur-containing extreme pressure or anti-wear agent is regarded as "highly-active" if the coupon weight loss in the above test is above 50 milligrams. If the weight loss is from 30 to 50 milligrams, the agent should be subjected to the planetary spur gear test in order to determine whether it is "highly active" or not.

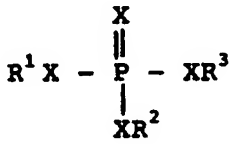
Generally speaking, sulphur-containing compounds which possess a linkage of two sulphur atoms (i.e., -S-S-) or four or more sulphur atoms (e.g., -S-S-S-S-, -S-S-S-S-S-, etc.) tend to be "highly active" in the sense used herein. In some cases a product from one manufacturer, for example sulphurised isobutene, may be "highly active" whereas a similar product from another manufacturer may not be "highly active". Thus in cases where the activity of a given sulphur-containing extreme pressure or anti-wear agent is not known with certainty, it is desirable to perform a test such as the planetary spur test to ascertain whether it is "a highly active" material in the sense of the present invention.

One preferred class of such agents is made by reacting an olefin such as isobutene with sulphur. The product, e.g. sulphurized isobutene, typically has a sulphur content of about 10 to about 50%, preferably 30 to 50%, by weight. A wide variety of other olefins or saturated hydrocarbons may be used in place of the isobutene.

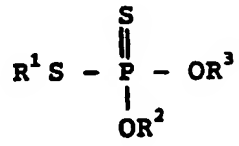
Other examples of sulphur-containing extreme pressure agents which may be used in the compositions of the invention are sulphur and the sulphur- and phosphorus-containing additives already mentioned, especially the thiophosphates and dithiophosphates, e.g. zinc dialkyl or diaryl dithiophosphates or trihydrocarbyldithiophosphates, customarily included in lubricant compositions as extreme pressure or anti-wear agents.

The compositions of the present invention may contain, as an extreme pressure or anti-wear agent, an

ester of a pentavalent acid of phosphorus, such as a fully or partially esterified phosphoric, phosphonic or pyrophosphoric acids or a sulphur-containing analog thereof. Such compounds have the formula:



wherein each of R^1, R^2 and R^3 is, independently, hydrogen or a hydrocarbyl group, provided that at least one of R^1, R^2 and R^3 is hydrocarbyl, and each X is oxygen or sulphur, at least one X preferably being sulphur. Most preferred are compounds of the formula



where at least 95 percent of the R^1 groups are hydrocarbyl groups, the balance, if any, being hydrogen atoms, and R^2 and R^3, when hydrocarbyl, can be aromatic, cycloaliphatic, and/or aliphatic hydrocarbon groups, or any combination of these. Preferably R_1, R_2 and R_3 are saturated or substantially saturated aliphatic, cycloaliphatic or polycycloaliphatic groups, such as alkyl, alkenyl, cycloalkyl, cycloalkenyl, cycloalkylalkyl, cycloalkylalkenyl, cycloalkenylalkyl, cycloalkenylalkenyl, and the like. As far as chain length or carbon atom content is concerned, the only requirement is that the hydrocarbyl groups are such that the compound is soluble in the base oil to at least the desired use concentration at ambient temperatures. The hydrocarbyl groups can contain functional substituents or non-hydrocarbon component groups which do not materially alter the predominantly hydrocarbon character of the hydrocarbyl groups themselves.

Because of the toxicity and disagreeable odour of hydrogen sulphide, it is desirable to use a highly active sulphur-containing extreme pressure or anti-wear agent that yields less than 500 ppm of vapour space H_2S when heated by itself for one week at 65° C.

The proportion of sulphur-containing extreme pressure or antiwear agent included in the compositions of the invention is preferably such that the molar ratio of the sulphur in the said sulphur-containing extreme pressure or anti-wear agent to the amino nitrogen in the amine or amino acid is from 40:1 to 5:1, and is typically 1.7 to 10% by weight, usually 2-4%, based on the weight of the lubricant.

In calculating the proportion of sulphur, the total sulphur content of the extreme pressure or antiwear agent should be taken into account, even though some of the sulphur in the agent may not qualify as "highly active" in the strict sense explained above.

The new compositions preferably contain a phosphorus-containing extreme pressure or antiwear agent. As already indicated the sulphur-containing agent may itself contain phosphorus, or a separate phosphorus-containing agent may be used with the sulphur-containing agent (which may itself contain phosphorus). Such separate phosphorus-containing agents include derivatives of phosphorus oxyacids and of poly-phosphorus oxyacids such as phosphites, phosphates and pyrophosphates, and especially their oil-soluble esters, acid esters and amine salts. Preferably a mono- or di-hydrocarbyl phosphite or phosphate or a mixture thereof is used, where the hydrocarbyl groups may be alkyl, alkenyl, phenyl, alkylphenyl or dialkylphenyl. Examples of suitable esters are monomethyl, dimethyl, mono-n-butyl, di-n-butyl, mono-isobutyl, di-isobutyl, monoamyl, diamyl, di-n-octyl, di-(2-ethyl-n-hexyl), monooleyl, dioleyl, monophenyl, diphenyl and di(dodecylphenyl) phosphite and phosphate, and their amine salts. Such phosphorus-containing agents are usually included in the new compositions in a proportion of 0.01 to 3.5% based on the weight of the lubricant. The compositions of the invention may also contain an alkali metal borate, e.g. sodium or potassium borate, e.g. in a proportion of 0.5 to 8% by weight of the lubricant.

The acid used in the new compositions is a weak acid, preferably one having a pKa of greater than about 2.0, and is usually a carboxylic acid in which one or more carboxyl groups are attached to a hydrocarbon radical of 1 to 100, preferably 2 to 36 carbon atoms. Other weak acids, e.g. a boric acid such as H_3BO_3 or metaboric acid, may also be used, e.g. in a amount from 0.1 to 8.0% by weight of the lubricant. Examples of suitable acids are alkanoic and alkenoic mono-, di- or poly-carboxylic acids of 1 to

100, preferably 2 to 54, carbon atoms, e.g. acetic acid, n-octanoic acid, decanoic acid, myristic acid, oleic acid, linoleic acid, tetrapropenylsuccinic acid, azelaic acid, or dimerised or trimerised linoleic acid. The acid used must be such as to form an oil-soluble salt with the amine used. Acyclic monocarboxylic acids are preferred.

Any amine may potentially be used in the compositions of the present invention. Preferred amines are aliphatic mono and polyamines containing 2 to 22 carbon atoms per molecule. Primary, secondary and tertiary amines are all suitable. Especially preferred amines are linear or branched aliphatic, cycloaliphatic or ethylenically unsaturated aliphatic amines of 6 to 22 carbon atoms, e.g. n-octylamine, oleylamine, or cyclohexylamine, polyethylene polyamines such as triethylene tetramine, and the tertiary alkyl primary amines sold under the trade names Primene 81-R and Primene JM-T. As already noted, the amine must be capable of forming an oil-soluble salt with the acid used.

The combined proportions of the carboxylic acid and of the amine used may be from 0.15 to 20.0% by weight of the lubricant, preferably 0.15 to 2.0%, and especially about 0.3%, but their respective amounts depend as already indicated on their molecular weights and the mole equivalence of the particular acid and amine used. In relation to the sulphur containing extreme pressure or antiwear agent the total amount of acid plus amine is typically 5 to 300%, preferably 20 to 100%, by weight.

In calculating the proportion of amino nitrogen in the compositions of the present invention, only free amine or amine salified with a weak acid should be taken into account. For example any amine salified with a phosphorus acid such as a dialkyl acid phosphate or phosphite is too tightly bound to be available for securing the improved results of the compositions of the present invention, and thus although such amine salts may be present in the compositions of this invention, the amount of amino nitrogen in such amine salts should not be considered as amino nitrogen in calculating the proportion of the latter in the compositions of the invention.

Instead of a mixture of acid and amine, an amino-acid may be used in the same total amount as a percentage based on the weight of the lubricant. Suitable amino-acids include glycine, alanine, and phenylalanine.

One measure for determining that the correct proportion of amine has been used in the new compositions in relation to the acid is a determination of the pH of the composition. Since the compositions consist essentially of a solution of various organic compounds normally in an oil which is usually a hydrocarbon oil, the compositions have, in a strict sense, no pH. However, it has been found that if a sample of the composition is diluted in a mixture of methanol and toluene and then assayed with a conventional pH probe as used in aqueous systems, a measurement is obtained which provides a useful measure of the relative proportions of basic and acidic materials present in the composition. Measured in this way, the pH of the compositions of the invention should be in the range of 3 to 10 or preferably of 7 to 9.

The compositions of the invention may contain other additives suitable for use in gear oils, for example:

Antioxidants

Zinc dialkyldithiophosphates, zinc diaryldithiophosphates, hindered phenols, amines and various organic compounds containing nitrogen, sulphur or phosphorus.

Antifoamants and demulsification agents

Silicone based fluids, ethylene glycol-propylene glycol condensation products, polyalkylacrylates.

Dispersants

Polyalkenyl succinimides, succinate esters, N-vinyl-pyrrolidone-methacrylate ester copolymers, fatty acid esters and fatty acid amides, and carboxylic acid derivative compositions (e.g. succinimides, succinic acid esters, succinic acid ester-amides, etc.) that have been post-treated by reaction with one or more post-treating reagents such as boron oxide, boron oxide hydrate, boron halides, boron acids, esters of boron acids, carbon disulphide, hydrogen sulphide, sulphur, sulphur chloride, alkenyl cyanides, carboxylic acid acylating agents (e.g. maleic anhydride, maleic acid, fumaric acid, malic acid, azelaic acid, adipic acid, C1 to C30 alkenyl succinic acids, C1 to C30 alkenylsuccinic anhydrides, etc.), aldehydes, ketones, urea, thiourea, guanidine, dicyandiamide, hydrocarbyl phosphates, hydrocarbyl phosphites, hydrocarbyl thiophosphates, hydrocarbyl thiophosphites, phosphorus sulphides, phosphorus oxides, phosphoric acid, phosphorous acid, hydrocarbyl thiocyanates, hydrocarbyl isocyanates, hydrocarbyl isothiocyanates, epoxides, episulphides, formaldehyde or formaldehyde producing compounds plus phenols, and sulphur plus phenols.

Detergents

Metal salts of organic salicylates, sulphonates, phenates or phosphonates.

Viscosity index improvers or pour point depressants

Polyalkylmethacrylates or olefin copolymers.

Friction Modifiers

Alkyl or alkenyl fatty acid amides, alkyl or alkenyl succinimides, or alkyl or alkenyl phosphonates.

The invention includes within its scope lubricant additive concentrates comprising 5 to 95% of one or more sulphur-containing extreme pressure or anti-wear agents, from 0.5 to 20% of a weak acid and from 1 to 20% of an amine, or from 0.5 to 25% of an amino acid, and a diluent oil, the said percentages being by weight based on the total weight of the concentrate, the amount of said acid being from 0.2 to 2 equivalents per equivalent of the said amine. Such concentrates may also contain 1 to 50% of one or more phosphorus-containing extreme pressure or anti-wear agents.

The compositions of the invention can conveniently be made by modification of existing compositions by adding appropriate amounts of acid and amine thereto.

The following Examples illustrate the invention.

EXAMPLES 1-3

The ingredients listed below were incorporated in an SAE 80W90 mineral oil of North Sea origin. The percentages by weight of each ingredient in the base oil is given.

	Example 1		Example 2		Example 3	
Sulphurised Isobutylene						
HiTEC 312 (45±3%S)	3.9	3.9	-	-	-	-
HiTEC 309 (45±3%S)	-	-	3.9	3.9	-	-
Anglamol 33 (45±3%S)	-	-	-	-	3.9	3.9
2-Ethylhexyl-acid phosphate/oleylamine salt	0.36	0.36	0.36	0.36	0.36	0.36
Copper Deactivator	0.07	0.07	0.07	0.07	0.07	0.07
Antifoam	0.06	0.06	0.06	0.06	0.06	0.06
Octanoic Acid		0.5		0.5		0.5
n-Octylamine	-	0.6	-	0.6	-	0.6

These blends contain 12.1 moles of sulphur per mole of amino nitrogen in the n-octylamine salt and 0.77 equivalents of octanoic acid per equivalent of n-octylamine.

EXAMPLE 4

A lubricating fluid of SAE 90 grade viscosity characteristics was blended with sulphurised isobutylene (2.2% w/w), an alkylamine/alkylphosphate/alkylphosphite/alkylthiophosphate mixture (0.5% w/w), and octanoic acid in a proportion such that there were approximately 135.6 moles of sulphur per mole of said acid. The sulphurised isobutylene itself contained 45% sulphur (w/w). The alkylamine is entirely neutralised by the phosphorus acids present.

This fluid was tested using the planetary spur gear test described below in which it gave 40 hours satisfactory running performance before excessive gear damage was observed. This test was repeated twice giving an average result of 44 hours.

A sample of the fluid described above was then treated with an n-octylamine/n-octanoic acid mixture (in equivalent amounts; 0.3% w/w) and then subjected to the same planetary spur gear test. The fluid contained about 38.2 moles of sulphur per mole of amino nitrogen, apart from the nitrogen sulphurised by the phosphorus acids, and 0.9 equivalents of octanoic acid per equivalent of amino nitrogen. This gave a performance of over 75 hours before excessive gear damage was observed.

The Planetary Spur Gear Test

In this test a system of spur-type gears is driven under variable and very heavy loads. The lubricating

fluid is circulated around the system by a pump and is maintained at between 95°C and 130°C. Samples of the lubricating fluid are removed periodically and analysed for iron content. The test is terminated when excessive wear is recorded either by high iron levels in the oil, or by gear tooth breakage. Lubricating fluids produced in accordance with the present invention are capable of enabling at least 60 and in preferred embodiments over 75 hours of running time in the test.

EXAMPLE 5

A sample of the first lubricating fluid described in Example 4 was treated with an acetic acid/oleylamine mixture (0.11% w/w acetic acid; 0.54% w/w oleylamine), and then subjected to the planetary spur gear test. The fluid contained approximately 23 moles of sulphur per mole of amino nitrogen, other than that salified by the phosphorus acids, and 0.95 equivalents of acetic acid per equivalent of amino nitrogen. Satisfactory performance of over 60 hours was obtained.

EXAMPLE 6

A sample of the first lubricating fluid described in Example 4 was treated with a mixture of tetrapropenylsuccinic acid and triethylenetetramine (0.22% w/w acid and 0.04% w/w amine), and then subjected to the planetary spur gear test. The fluid contained approximately 29.4 moles of sulphur per mole of amino nitrogen other than that salified by the phosphorus acids. Satisfactory performance over [illegible] hours was obtained.

Claims

1. A lubricant composition comprising a lubricant, 1 to 20% by weight of one or more sulphur-containing extreme pressure or anti-wear agents, from 0.1 to 10% by weight of a weak acid and from 0.05 to 10% by weight of an amine, or from 0.15 to 20% by weight of an amino-acid, the said percentages being based on the weight of the lubricant, the amount of the said acid being from 0.2 to 2 equivalents per equivalent of the said amine, and the salt of the said acid with said amine being soluble in the said lubricant.

2. A composition according to claim 1 containing 0.67 to 1.25 equivalents of the said acid per equivalent of the said amine.

3. A composition according to claim 1 or 2 in which the molar ratio of the sulphur in the said sulphur-containing extreme pressure or antiwear agent to the amino nitrogen in the said amine or amino acid is from 40:1 to 5:1.

4. A composition according to any one of claims 1 to 3 containing 1.7 to 10% by weight of the lubricant of the said sulphur-containing extreme pressure or anti-wear agent.

5. A composition according to any one of claims 1 to 4 in which the said sulphur-containing extreme pressure or anti-wear agent contains 30 to 50% by weight of sulphur.

6. A composition according to claim 5 in which the said sulphur-containing extreme pressure or antiwear agent is sulphur, a sulphurized olefin, sulphurized ester, sulphurized fatty acid, or dialkylpolysulphide.

7. A composition according to claim 6 in which the said agent is sulphurized isobutene.

8. A composition according to any of claims 1 to 4 in which the sulphur-containing extreme pressure or anti-wear agent is a dialkyldithiophosphate or another sulphur-containing phosphite or phosphate ester or salt.

9. A composition according to any of claims 1 to 7 which also contains 0.01 to 3.5% by weight of the lubricant of a phosphorus-containing extreme pressure or anti-wear agent.

10. A composition according to claim 9 in which the said phosphorus-containing agent is a mono- or di-hydrocarbyl phosphite or phosphate or a mixture thereof wherein the said hydrocarbyl is alkyl, alkenyl, phenyl, alkylphenyl or dialkylphenyl.

11. A composition according to any one of claims 1 to 10 which also contains 0.1 to 8% by weight of the lubricant of an alkali metal borate.

12. A composition according to any one of claims 1 to 11 in which the amine is a linear or branched aliphatic, cycloaliphatic, or linear or branched ethylenically unsaturated aliphatic amine of 6 to 22 carbon atoms, or a polyethylene polyamine.

13. A composition according to claim 12 in which the amine is n-octylamine, oleylamine, or triethylenetetramine.

14. A composition according to any one of claims 1 to 12 in which the said acid is a carboxylic acid with a pKa greater than 2.

15. A composition according to claim 14 in which the said acid is an alkanoic or alkenoic mono- or di- or poly-carboxylic acid of 2 to 54 carbon atoms.

16. A composition according to claim 15 in which the said acid is acetic acid, n-octanoic acid, decanoic acid, myristic acid, oleic acid, linoleic acid, tetrapropenylsuccinic acid, azelaic acid, or dimerized or trimerized linoleic acid.

17. A composition according to any one of the preceding claims which also contains one or more of antioxidants, antifoamants or demulsification agents, dispersants, detergents, viscosity index improvers, pour point depressants and friction modifiers.

18. A lubricant additive concentrate comprising 5 to 95% of one or more sulphur-containing extreme pressure or anti-wear agents, from 0.5 to 20% of a weak acid and from 1 to 20% of an amine, or from 0.5 to 25% of an amino acid, and a diluent oil, the said percentages being by weight based on the total weight of the concentrate, the amount of the said acid being from 0.2 to 2 equivalents per equivalent of the said amine.

19. A lubricant additive concentrate according to claim 18 which also contains 1 to 50% of one or more phosphorus-containing extreme pressure or anti-wear agents.